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## (54) Method for reinforcement or permanent deformation of hair

(57) A method for the reinforcement and/or permanent deformation of hair, in which, in a first stage, the hair is subjected to the action of a reducing agent to break the disulphide linkages of the keratocystine to form thiol groups, and in a second stage, a modifying agent, which is a polyhaloacetylated polymer comprising a halogen which is capable of reacting with the thiol groups, is applied to the hair.

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METHOD FOR REINFORCEMENT OR PERMANENT DEFORMATION OF HAIR

The subject of the present invention is a new method for the reinforcement and/or permanent deformation of hair, as well as a composition intended for implementing this method.

5 It is known that the reinforcement of hair and its maintenance in a given shape by impregnating it with a solution of a polymer which leaves, after drying, a film which ensures the provision of an increased cohesiveness and an increased stability to the temporary deformation of the hair obtained, for example, using the so-called hair setting method is conventional.

10 Such polymers have an action which is simply mechanical, because they form a flexible sheath around the hair, which enables the return to natural shape to 15 be delayed.

The use of the so-called restructuring agents such as methylol derivatives which penetrate into the hair fibre and become polymerized therein, which gives an increased rigidity to the hair, is also known.

20 A method called the permanent deformation of hair, which is based on a combination of a mechanical deformation and a chemical modification of the hair is also known. More specifically, the hair is subjected to a first chemical modification which consists in breaking 25 some disulphide linkages of the keratin molecule, the said disulphide groups being converted into thiol groups, which results in the fibre being rendered temporarily

plastic, i.e. deformable without elasticity. The hair is then subjected to an imposed mechanical deformation (winding round curlers or smoothing the hair) and the hair is then subjected to a second chemical modification 5 which consists especially in forming again, by oxidation, disulphide linkages from thiol groups. Because of the deformation imposed on the hair, the new linkages are formed at sites other than those of the original linkages, which results in the hair lock being set in the new shape 10 which is imposed on it.

The subject of the present invention is a new method which enables the hair to be reinforced as well as subjected, if desired, to a permanent deformation. This permanent deformation may be a curling as well as a 15 straightening or defrizzing.

The process of the invention comprises, as in the case of conventional cold permanent-waving operation, a hair reduction stage and is characterized by the application, in a second stage, of a polymer capable of forming 20 covalent bonds with the thiol groups of the reduced hair. As a result, the polymer is chemically bound to the hair and serves as reinforcing agent. Additionally, when the hair is subjected to a mechanical deformation at the time when the polymer is applied, it retains the shape imposed 25 on it at the time of this application.

A reinforcement of the hair which proves to be particularly advantageous in the case of fine hairs or

sensitized hair, i.e. having undergone treatments producing a degrading effect on the hair (for example dyeing).

Additionally, one of the advantages of using a polymeric reagent is that such reagents are not capable  
5 of penetrating into the scalp and possibly causing toxicity problems.

Therefore, the subject of the present invention is a method for the reinforcement and/or permanent deformation of hair, in which, in a first stage, the hair is  
10 subjected to the action of a reducing agent so as to break the disulphide linkages of keratocystine in order to form thiol groups, and then, in a second stage, a modifying agent which promotes the formation of new chemical linkages with the thiol groups is applied to  
15 the hair, characterized in that the said modifying agent is a polyhaloacetylated polymer, the halogen of which is capable of reacting with the thiol groups.

The first stage of the method which consists in opening the S-S linkages of keratin, with a composition  
20 containing a reducing agent, is a reaction known per se and the reducing agents which can be employed as well known to permanent hair deformation specialists.

Similarly, the formulation of reducing compositions capable of accomplishing this first stage is known  
25 and described in books on cosmetology, such as, for example, "Problèmes capillaires" (Hair problems) by E. SIDI and C. ZVIAK, Paris (1966).

The formulation of such reducing compositions, which does not form part of the invention, will not therefore be described in detail below. In general, reducing compositions contain a reducing agent such as, for example, a mercaptan, an alkali metal or ammonium sulphite or bisulphite, thioglycolic acid, thiolactic acid or alternatively a thioglycolic or thiolactic acid ester (for example glycerol or glycol monothioglycolate), the said composition generally having a pH of between 7 and 10, and preferably between 8 and 9.5. The reducing agent is preferably present in the reducing composition at a concentration from 2 to 25% by weight relative to the total weight of the said composition.

In the first stage of the method, reduction levels of between 5 and 30% can be achieved.

The basic pH of the reducing compositions is generally obtained using alkaline agents such as, for example, ammonia, monoethanolamine, diethanolamine, triethanolamine and the like.

In particular embodiments, the method of the invention may also have the following features, considered in isolation or in combination:

the polyhaloacetylated polymer is allowed to act on the reduced hair for a period which may vary, for example, from 10 to 45 minutes; this is preferably carried out at a temperature from 25 to 70°C; the hair is then rinsed with water and dried if desired; and

the polyhaloacetylated polymer is applied to  
the reduced hair which is subjected to a stretching (wind-  
ing round curlers or smoothing by combing), and then, after  
leaving the polymer to act for a sufficient period, the  
5 hair is rinsed and dried while still being maintained  
stretched; a permanent hair deformation, curling or  
straightening, as the case may be, is thus obtained.

According to a first variant, the polyhaloacety-  
lated polymer may be applied, if desired, in admixture  
10 with a conventional oxidizing agent such as, for example,  
hydrogen peroxide or, according to a second variant, af-  
ter applying the polyhaloacetylated polymer, which results  
in the second stage of the method according to the inven-  
tion optionally being completed in the case where some  
15 thiol groups still remain.

The polyhaloacetylated polymers employed in the  
method according to the invention are essentially charac-  
terized in that they all contain a halogen (chlorine or  
bromine, but preferably chlorine) on a carbon in the al-  
20 pha position relative to a carbonyl group.

These polymers which are polyhaloacetylated and  
preferably polychloroacetylated, may be obtained accord-  
ing to different methods.

In particular, they may be obtained by the homo-  
25 polymerization or the copolymerization of a haloacetyla-  
ted monomer carrying a polymerizable double bond; among  
the haloacetylated monomers, there will be mentioned, in

particular, the following: vinyl chloroacetate, allyl chloroacetate, vinyl chloroformate, N-allyl chloroacetamide, methyl 2-chloroacetamidoacrylate, N-chloroacetamido-methyl acrylamide, N-chloroacetamidomethyl methacrylamide,  
5 2-(chloroacetoxy)propyl methacrylate, 2-(chloroacetylcarbamoyloxy)propyl methacrylate, N-methacryloyl-N'-chloroacetylurea and the like; in the case of a copolymerization, a comonomer which promotes the solubility of the final copolymer in the solvent desired, which is generally  
10 by water or a water-alcohol mixture, is preferably chosen; among comonomers, there will be mentioned, in particular, the following: N-vinylpyrrolidone, N,N-dimethylacrylamide, N-acrylamidomethyl-2-oxopyrrolidone, 3-methacrylamidopropyl-1(N,N,N-trimethylammonium) chloride, methylacrylate,  
15 methylmethacrylate, N,N-dimethylacrylamide and the like.

The haloacetylated monomers are known and may be prepared according to known methods.

The polyhaloacetylated polymers may also be obtained by attaching a haloacetyl group to a polymer carrying amine or primary or secondary alcohol groups, the haloacetyl group being attached in a known manner (described for example in French Patent 1,149,161 or in the article by A. Carrov et al., Die Angewandte Makromolekulare chemie, 24 1972, No. 322, 101-120) which consists in reacting a haloacetyl halide, preferably chloroacetyl chloride, with the said polymer carrying amine or alcohol groups; among the polymers which may be employed for this

haloacetylation reaction; there may be mentioned, in particular: polyvinyl amine, polyvinyl alcohol, 2-hydroxyethyl polyacrylate, polylysine, copolymers obtained by condensing 2,2-dimethyl-1,3-diaminopropane with methylene-  
5 bisacrylamide, water-soluble protein hydrolysates and the like.

The polyhaloacetylated polymers employed according to the invention preferably have a molecular weight generally of between 500 and 50,000.

10 Although some of the homopolymers and copolymers are known, examples for the preparation of some of them as well as examples for the preparation of the haloacetylated monomers will be given below.

Among the homopolymers and the polyhaloactylated 15 copolymers which are particularly preferred for implementing the method, the following may be mentioned:

N-vinylpyrrolidone/vinyl chloroacetate copolymer,

20 methyl 2-chloroacetamidoacrylate/N-acrylamido-

methyl-2-oxopyrrolidine copolymer,

methyl 2-chloroacetamidoacrylate homopolymer,

N-chloroacetamidomethyl acrylamide/N-acrylamido-

methyl-2-oxopyrrolidine copolymer,

methyl 2-chloroacetamidoacrylate/methacrylamido-

25 propyl trimethylammonium chloride copolymer,

N-chloroacetamidomethyl acrylamide/methyl acry-

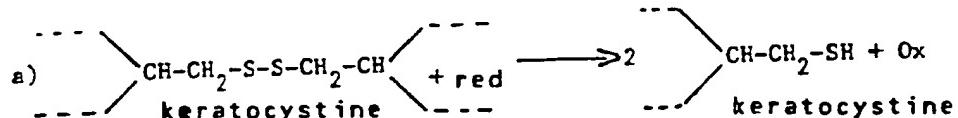
late copolymer,

N-chloroacetamidomethyl acrylamide homopolymer,  
and

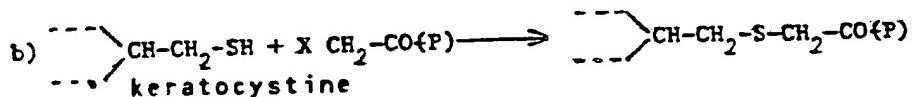
N-chloroacetamidomethyl acrylamide/methacrylamido-  
propyl trimethylammonium chloride copolymer.

5 According to the process of the invention, the polyhaloacetylated polymer is applied to the reduced hair using a composition preferably having a pH of 8 to 9.5, or alternatively the hair is rinsed beforehand with a buffer solution having such a pH.

10 The method of the present application may therefore be explained diagrammatically using the following chemical reactions:



Red and Ox representing the reduced and the  
15 oxidized forms of an oxidation-reduction system respectively and,



in which X represents halogen and (P) denotes the rest of the polymer.

A composition intended for implementing the method as defined above also forms the subject of the  
20 present invention.

This composition is mainly characterized in that it contains, in a suitable vehicle, at least one poly-haloacetylated polymer as defined above.

In the composition of the invention, the poly-haloacetylated polymer is generally present at concentrations which may range from 0.5 to 10 % by weight relative to the total weight of the composition.

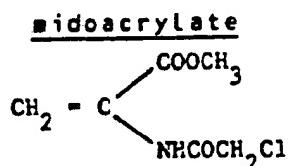
The compositions of the invention may be present, in particular in the form of aqueous or aqueous/alcoholic solutions, the alcohol being, in particular, a lower alkanol such as ethanol or isopropanol, or in the form of creams, gels, emulsions, aerosols and the like.

The compositions of the invention may additionally contain various common ingredients such as pH-modifying agents, perfumes, dyestuffs, preservatives, thickeners, surfactants, other cosmetic polymers and the like.

The following examples illustrate the invention without, however, limiting it.

20 I. Preparation of haloacetylated monomers

EXAMPLE Ia: Preparation of methyl 2-chloroacetamidoacrylate



163.5 g of 2-chloroacetamidoacrylic acid prepared according to J.P. Greenstein, Arch. Biochem. 1947, 14, 249 are added, in the course of one hour and

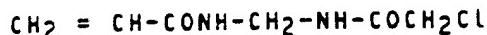
maintaining the temperature at 10°C, to 40 g of sodium hydroxide dissolved in 250 ml of water and a solution of 170 g of silver nitrate in 1,500 ml of water is then introduced. The white solid formed is filtered, washed with water and then with acetone, drained and transferred into a reactor. 1,000 g of methyl iodide and 1 g of hydroquinone monomethyl ether are then added and the mixture is maintained under reflux for two hours. After filtering and concentrating the reaction mixture, 134 g of an oily product which crystallizes (melting point: 42°C) in a mixture of 130 ml of water and 220 ml of methanol are obtained.

	Elemental analysis:	<u>Calculated</u>	<u>Found</u>
	C	40.56 %	40.69 %
15	H	4.51 %	4.61 %
	N	7.89 %	7.68 %
	O	27.04 %	26.77 %
	Cl	20.00 %	20.13 %

<sup>1</sup>H NMR spectrum at 90 MHz in CHCl<sub>3</sub>:

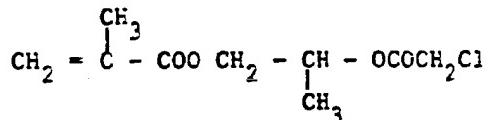
20 -CH<sub>2</sub>Cl δ = 4.1 ppm

EXAMPLE 1b: Preparation of N-chloroacetamidomethyl acrylamide



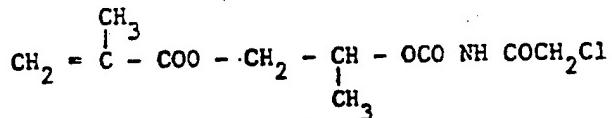
This product is prepared by reacting hydroxy-  
25 methyl chloroacetamide with acrylamide in formic acid,  
according to the process described by E. Müller, Die  
Angew. Makr. Chem. 1972, 7, 99

EXAMPLE 1c: Preparation of 2-(chloroacetoxy)-  
propyl methacrylate



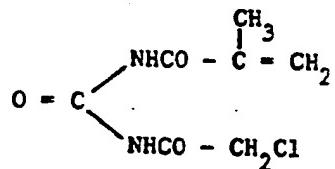
This product is prepared according to the literature reference cited in Example 1b, by reacting 5 chloroacetic acid with 2-hydroxypropyl methacrylate.

EXAMPLE 1d: Preparation of 2-(chloroacetylcarbamoyloxy)propyl methacrylate



This product is obtained starting with chloro-  
methylcarbonyl isocyanate and 2-hydroxypropyl methacrylate  
according to the same literature reference.

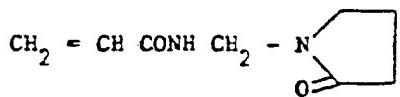
EXAMPLE 1e: Preparation of N-methacryloyl-N'-chloroacetylurea



This product is prepared according to the same reference starting with methacrylamide and chloromethyl-  
15 carbonyl isocyanate.

**EXAMPLE 2:**

Preparation of the N-acrylamidomethyl-2-oxo-pyrrolidine comonomer



This monomer is synthesized according to  
B. Sebillie, C.R. Acad. Sci., Serie C. 1969, 269, 1513.

EXAMPLE 3: Preparation of the haloacetylated polymers  
by polymerizing the haloacetylated monomers

5       EXAMPLE 3a: N-vinylpyrrolidone/vinyl chloroacetate  
copolymer

63.2 g of N-vinylpyrrolidone, 36.8 g of vinyl chloroacetate, 200 g of ethanol and 1 g of azobis-isobutyronitrile are introduced into a 1 litre reactor.

10      The mixture, which is maintained stirred under a nitrogen atmosphere, is heated under reflux for 8 hours. The crude polymer solution is diluted in 200 g of acetone and precipitated in 5 litres of ethyl ether. After filtering and drying, a polymer containing, according to  
15      chlorine determination, 37.5 % of vinyl chloroacetate  
is obtained.

EXAMPLE 3b: Methyl 2-chloroacetamidoacrylate/  
N-acrylamidomethyl-2-oxopyrrolidine  
copolymer

20      93.8 g of methyl 2-chloroacetamidoacrylate,  
31.2 g of N-acrylamidomethyl-2-oxopyrrolidine, 3.5 litres  
of methanol and 50 g of a 33 % hydrogen peroxide solution  
are introduced into a 4 l photochemical reactor equipped  
with a 2,000W lamp (ref. Q 2020 Original Hanau). The  
25      solution, which is heated to 50°C, is irradiated for 6

hours. The reaction mixture is filtered, the solution concentrated to 400 g and poured into 5 litres of ethyl ether. The polymer recovered is dried (weight obtained: 93 g). The water-soluble part is obtained by extracting 5 with 1.8 litres of water at 50°C. 68 g of water-soluble polymer are then obtained.

Elemental analysis: Found

C 42.22

H 6.08

10 N 12.21

O 28.47

CL 10.15

which shows a 54 % incorporation of the chlorinated monomer.

15        EXAMPLE 3c: Methyl 2-chloroacetamidoacrylate homopolymer

The following are introduced into a HANOVIA photochemical reactor equipped with a 100W medium pressure lamp sold by PROLABO:

20        25 g of methyl 2-chloroacetamidoacrylate  
            33.2 g of a 33 % hydrogen peroxide solution  
            610 g of methanol

The solution, which is maintained at 20°C, is irradiated for 8 hours. The reaction mixture is filtered, 25 concentrated to 100 g and poured into 2 litres of ethyl ether, with stirring; after filtering, the polymer obtained is dried; 4.3 g of the expected polymer is obtained.

Elemental analysis:	Found	Calculated
C	40.35	40.56
H	4.61	4.51
N	7.80	7.89
O	26.92	27.04
Cl	20.34	20.00

5

10

EXAMPLE 3d: Methyl 2-chloroacetamidoacrylate/  
methacrylamidopropyl trimethyl-  
ammonium chloride (sold by TEXACO  
(USA) under the trade name MAPTAC)  
copolymer

The following are introduced into a tubular  
photochemical reactor equipped with a HANOVIA 100W medium  
pressure lamp:

15      4 g of methyl 2-chloroacetamidoacrylate  
          2 g of a 50 % solution of MAPTAC in water  
          6.66 g of a 50 % hydrogen peroxide solution  
          122 g of methanol.

20      This solution, which is maintained at 20°C, is  
          irradiated for 6 hours at 20°C. After filtering, the  
          reaction mixture is concentrated to 15 g and precipitated  
          in 500 ml of ethyl ether. 3.2 g of water-soluble polymer,  
          characterized by <sup>1</sup>H NMR spectroscopy at 250 MHz  
          (Solvent DMSO), are obtained.

25      Integration of the characteristic peaks shows  
          a 30 % incorporation of the chlorinated monomer.

EXAMPLE 3e: N-chloroacetamidomethyl acrylamide/methyl acrylate copolymer

10 g of N-chloroacetamidomethyl acrylamide,  
40 g of methyl acrylate, 400 g of a 50:50 water:ethanol  
5 mixture and 0.25 g of azobis-iso-butyronitrile are in-  
troduced into a reactor. The solution is adjusted to  
pH = 2.5 with 0.1N hydrochloric acid and heated at 70°C  
for 6 hours. After separating the polymer by phase separa-  
tion, the latter is redissolved in 200 g of ethyl acetate  
10 and precipitated using 5 litres of hexane. After filtering  
and drying, 24 g of polymer which is soluble in a 90:10  
ethanol:water mixture are obtained.

Elemental analysis: Found

C 51.38

15 H 6.67

N 7.71

O 24.24

CL 6.70

which shows a 33 % incorporation of the chlorinated  
20 monomer.

EXAMPLE 3f: N-chloroacetamidomethyl acrylamide homopolymer

2 g of N-chloroacetamidomethyl acrylamide,  
8 g of absolute ethanol and 8 g of water are introduced  
25 into a reactor; the pH of this solution is adjusted to  
2.4 with 0.1M HCl, 0.1 g of azobis-iso-butyronitrile is  
added and the mixture is heated for 2 hours, the solvent

being refluxed. The polymer, which is soluble in the hot reaction medium, precipitates on cooling to 20°C. It is then recovered and dried.

Elemental analysis: Found

5                   C 40.83  
                    H 5.34  
                    N 14.19  
                    O 24.62  
                    CL 14.92

10                  EXAMPLE 3g: N-chloroacetamidomethyl acrylamide/  
                     methacrylamidopropyl trimethylammonium  
                     chloride (MAPTAC) copolymer

144 g of N-chloroacetamidomethyl acrylamide, 72 g of a 50 % MAPTAC solution in water, 720 g of ethanol, 684 g 15 of water and 9 g of azobis-iso-butyronitrile are introduced into a reactor.

The mixture is heated, with stirring and under a nitrogen atmosphere, for 4 hours, the solvent being refluxed; at the end of the polymerization, the solvent is 20 removed using a rotary evaporator until a syrup is obtained and precipitation is then carried out in 10 litres of acetone. The solid residue is dried in an oven under reduced pressure at 40°C. 180 g of pure polymer are obtained.

Elemental analysis: Found

C 42.2

H 6.5

N 14.4

5 O 19.7

CL 16.9

which shows an incorporation of 67.5 % of the chlorinated monomer and 32.5 % of MAPTAC.

EXAMPLE 3h: N-chloroacetamidomethyl acrylamide/

10 N-acrylamidomethyl-2-oxopyrrolidine  
copolymer

18 g of N-chloroacetamidomethyl acrylamide,  
18 g of N-acrylamidomethyl-2-oxopyrrolidine, 144 g of  
ethanol, 144 g of water and 1.8 g of azobis-iso-butyro-  
15 nitrile are introduced into a reactor. The mixture,  
which is maintained stirred under a nitrogen atmosphere,  
is heated for 2 hours, the solvent being refluxed.

After cooling, the reaction mixture is concentrated using a rotary evaporator until a weight of  
20 110 g is obtained and then diluted with 70 ml of acetone.

The solution is then precipitated in 5 Litres of acetone. The polymer is filtered and oven-dried under vacuum at 40°C.

Elemental analysis: Found

C 47.8

H 6.5

N 15.2

5 O 21.4

CL 8.9

which shows an incorporation of 50.4 % of the chlorinated monomer and 49.6 % of the comonomer.

10 EXAMPLE 3i: N-chloroacetamidomethyl acrylamide/methacrylamidopropyl trimethylammonium chloride (MAPTAC) copolymer

80 g of N-chloroacetamidomethyl acrylamide, 40 g of a 50 % solution of MAPTAC in water, 3 Litres of methanol and 50 g of a 33 % hydrogen peroxide solution are introduced 15 into a 4 litre photochemical reactor equipped with a 2,000 W lamp (ref. Q2020 Original Mayau). The solution, which is heated to 45°C, is irradiated for 4 hours. The reaction mixture is concentrated to 175 g and then poured into 4 litres of acetone. The polymer recovered is dried; it is 20 completely water-soluble.

Elemental analysis: Found

C 41.45

H 6.10

N 21.95

25 O 13.23

CL 16.82

which shows an incorporation of 63 % of the chlorinated

monomer and 37 % of MAPTAC.

EXAMPLE 3j: N-chloroacetamidomethyl acrylamide/  
N,N-dimethyl acrylamide copolymer

21 g of N-chloroacetamidomethyl acrylamide,

5 14 g of N,N-dimethylacrylamide, 850 g of methanol and  
42 ml of a 33 % hydrogen peroxide solution are introduced  
into a HANOVIA photochemical reactor equipped with a  
100 W medium pressure lamp. The solution, which is  
maintained at 20°C, is irradiated for 6 hours. The  
10 reaction mixture is concentrated to 50 g and then poured  
into 1 litre of diethyl ether. The polymer recovered is  
dried and it is completely water-soluble.

Elemental analysis: Found

C 45.90

15 H 6.90

N 13.64

O 23.19

Cl 10.41

which shows a 52 % incorporation of the chlorinated monomer.

20 EXAMPLE 3k: N-chloroacetamidomethyl acrylamide/  
methacrylaminopropyl trimethylammonium  
chloride (MAPTAC) copolymer

40 g of chloroacetamidomethyl acrylamide, 20 g of  
a 50 % solution of MAPTAC in water, 15 g of a 30 % hydrogen  
25 peroxide solution, 37.5 g of water and 100 g of isopropanol  
are introduced into a reactor. The mixture is heated under  
reflux and a solution of 5 g of ascorbic acid in 400 g of

water is then added in the course of 40 min. The refluxing of the solvent is maintained for 4 hours after the addition.

The reaction mixture is concentrated to a third and the polymer is precipitated in 3 litres of acetone.

5 The polymer recovered is dried under vacuum at 40°C.

Elemental analysis: Found

C 42.38

H 6.35

N 14.02

10 O 21.97

CL 15.43

which shows an incorporation of 74 % of the chlorinated monomer and 26 % of MAPTAC.

EXAMPLE 3L: N-chloroacetamidomethyl acrylamide/  
15 methacrylamidopropyl trimethylammonium  
chloride (MAPTAC) copolymer

28.8 g of chloroacetamidomethyl acrylamide, 14.4 g of a 50 % solution of MAPTAC, 685 g of isopropanol, 3.6 g of azobis-iso-butyronitrile and 3.6 g of dodecyl-20 mercaptan are introduced into a reactor. The refluxing of the solvent is maintained for 16 hours. The polymer precipitates partially on the walls of the reactor. The precipitated polymer is dissolved in 100 ml of methanol.

The reaction mixture is concentrated and the 25 polymer is precipitated in 2 litres of acetone.

Elemental analysis: Found

C 45.09

H 6.52

N 13.70

5 O 16.88

CL 17.7

which shows an incorporation of 82 % of the chlorinated monomer and 18 % of MAPTAC.

EXAMPLE 4: Preparation of a haloacetylated polymer

10 by binding a haloacetylated halide  
to a polymer

6.4 g of the polycondensate obtained by the  
polyaddition of 1,1-dimethyl-1,3-diaminopropane and  
methylenebisacrylamide according to the procedure  
15 described in French Patent No. 85/10,158, Example 2, are  
dissolved in 45 g of N-methylpyrrolidone and heated to  
50°C. 6 g of freshly distilled chloroacetyl chloride are  
added slowly to this solution. The reaction is carried  
out over 10 hours. The mixture obtained is precipitated  
20 in 1 litre of acetone, the polymer recovered, which is  
disolved in water, is adjusted to pH 9 with sodium  
bicarbonate, which brings about its precipitation. It  
is then filtered, washed and dried. 5 g of polymer  
soluble in a 50:50 water:ethanol mixture are obtained.

Elemental analysis: Found

C 48.60

H 6.24

N 14.00

5 O 17.40

Cl 12.7

which shows a 75 % incorporation of the chlorinated monomer.

EXAMPLE 5: Reaction of the polymer with the reduced hair

10

EXAMPLE 5a: Preparation of reduced hair

Natural hair is reduced using solutions containing 2 % of thioglycolic acid, at pH 9.5 (ammoniacal buffer), the reaction time being 30 minutes at 30°C.

15 Analysis of the hair shows a 20 to 30 % reduction rate (ratio of cysteine content after reduction to cystine content before reduction).

EXAMPLE 5b: Procedure for reacting the polymer with the reduced hair

20 The reduced hair is immersed in a polymer solution adjusted to pH 9 (buffer: NH<sub>4</sub>Cl 50 g, 900 ml of water, NH<sub>4</sub>OH d=0.92 to q.s. pH 9, water q.s. 1 l) and maintained at 30°C for 30 minutes, or alternatively, as a variant, the hair is reduced beforehand and rinsed with a buffer solution at pH 9, impregnated with the polymer solution and exposed for 30 minutes at 30°C. In both cases, the hair is subsequently rinsed and dried.

The drying may be carried out after winding the hair round curlers, under the drier.

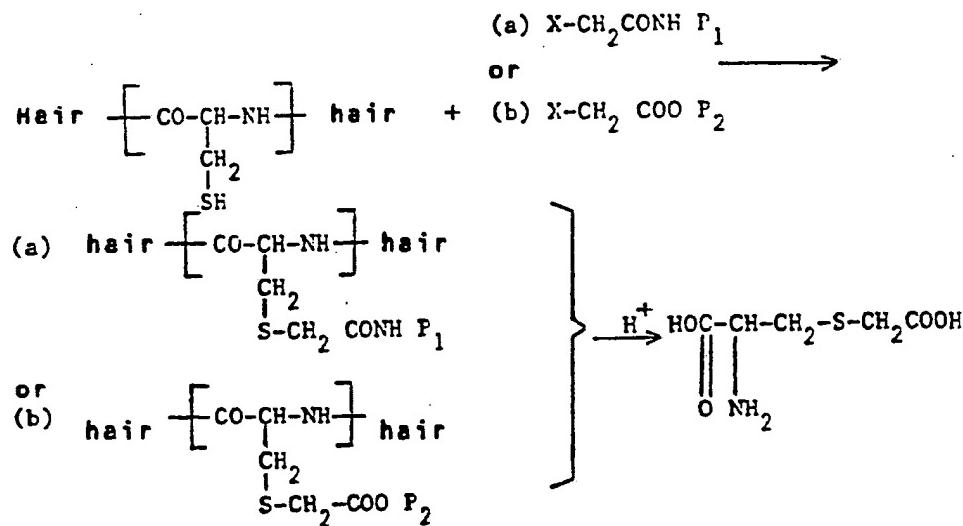
EXAMPLE 5c: Determination of the chemical modification caused in the hair after reacting with the polymer

5

### General procedure:

After treating with the polymers, the hair is subjected to an acid hydrolysis at 110°C in sealed tubes and the percentage of amino acids in the hydrolysate is determined using a TECHNICON TSM autoanalyzer.

The cysteine which is reacted with the halo-acetamide or the haloacetate group is converted to S-carboxymethylcysteine according to the following scheme:



15 X represents halogen and P<sub>1</sub> and P<sub>2</sub> the rest of the polymer.

EXAMPLE 6: Examples of treatment of reduced hair  
by the action of polyhaloacetylated  
polymers

EXAMPLE 6a:

5           The polymer of Example 3c is dissolved in a pH 9 buffer: ethanol (30:70) mixture.

Stoichiometric proportions between the cysteine present in the reduced hair and the chloroacetamido groups of the polymer are employed. 10 ml of solution containing 10 0.9 % of polymer are prepared to treat 300 mg of hair.

Based on hair reduction rate, the reaction yield varies from 27 to 56 %.

EXAMPLE 6b:

15          The polymer of Example 3b is reacted under conditions identical to those of the preceding example; however, in this case, a 1.8 % solution of the polymer in the ammoniacal buffer at pH 9 is prepared.

The reaction yields are between 36 and 68 % in the different tests.

20          EXAMPLE 6c:

The polymer of Example 3d is reacted under conditions identical to those of the preceding example.

The yields of reaction with the cysteine in the hair is then from 55 to 59 %.

25          EXAMPLE 6d:

The polymer of Example 4 is dissolved in a pH 9 ammoniacal buffer: ethanol (33:66) mixture, to a

concentration of 4.4 % and reacted with the reduced hair (0.058 mole of cysteine/100 g of hair).

After 30 minutes of reaction at 30°C, the reaction yield is 43 %.

5           EXAMPLE 6e:

The polymer of Example 3g is dissolved to 2.45 % in the ammoniacal buffer at pH 9 and reacted with cysteine on the one hand, and with the reduced hair on the other; after 30 minutes at 30°C, the reaction yields are 98 % and 10 65 % respectively.

EXAMPLE 6f:

The polymer of Example 3h is dissolved in the pH 9 ammoniacal buffer: ethanol (70/30) mixture and then reacted for 10 and 30 minutes at 30°C with cysteine in 15 stoichiometric quantities.

The reaction yields are 89 and 98 % respectively.

EXAMPLE 6g:

Example 6b is repeated; but, in this case, for the complete treatment of the head of hair by impregnation.

20           In this case, the rate of reduction of the hair by 0.3M thioglycolic acid at pH 9 is 5 % ( $6 \times 10^{-3}$  moles of cysteine present per 100 g of hair).

After reacting with the polymer of Example 3b, a sample of hair is taken and hydrolyzed. The determination of S-carboxymethylcysteine shows a yield of 25 to 25 30 % in this case.

EXAMPLE 6h:

The preceding example is repeated, but causing  
a greater reduction of 12.5 %.

After reacting with the polymer of Example 3b,  
5 reaction yield of 9 % is revealed.

EXAMPLE 6i:

The polymer of Example 3i is dissolved in the  
ammoniacal buffer at pH 9 and then reacted with the  
reduced hair, the reactive groups being in equimolecular  
10 quantities. After 30 minutes at 30°C, the reaction  
yield is 44 %.

EXAMPLE 6j:

The polymer of Example 3j is dissolved in the  
ammoniacal buffer at pH 9 and then reacted with the  
15 reduced hair, the reactive groups being in equimolecular  
quantities. After 30 minutes at 30°C, the reaction  
yield is 51 %.

CONCLUSION:

In general, after treating the reduced hair  
20 with the polyhaloacetylated polymers according to the  
method of the invention, it is observed that the whole  
rate of their cosmetic properties are improved. The  
following properties are more particularly improved:

retention of curls after the hair is wound round  
25 curlers; and  
ease of combing (better disentanglement).

Moreover, an improvement in the softness of

hair treated in this way is observed.

EXAMPLE 7: EXAMPLES OF COMPOSITIONS

The following compositions enable the method according to the invention to be implemented.

5           LOTIONS

Example 7a:

	Polymer according to Example 3c	0.9 g
	Ethanol	70.0 g
	Perfume	0.05g
10	Liquid ammonia q.s. pH 9	
	Water q.s.	100 g

In this example, the polymer according to Example 3c may be replaced by the same quantity of the polymer according to Example 3a.

15           Example 7b:

	Polymer according to Example 3b	1.8 g
	Ethanol	70.0 g
	Perfume	0.02g
	Liquid ammonia q.s. pH 9	
20	Water q.s.	100 g

In this example, the polymer according to Example 3b may be replaced by the same quantity of the polymer according to Example 3d.

Example 7c:

	Polymer according to Example 4	4.4 g
	Ethanol	66.0 g
	Perfume	0.04g
5	Liquid ammonia q.s. pH 9	
	Water q.s.	100 g

Example 7d:

	Polymer according to Example 3g	2.45g
	Perfume	0.05g
10	Liquid ammonia q.s. pH 9	
	Water q.s.	100 g

Example 7e:

	Polymer according to Example 3h	1 g
	Ethanol	30 g
15	Perfume	0.02g
	Liquid ammonia q.s. pH 9	
	Water q.s.	100 g

GEL

Example 7f:

20	Polymer according to Example 3i	5 g
	Hydroxymethylcellulose sold under the	
	tradename "NATROSOL HHR 250" by HERCULES	3 g
	Perfume	0.03g
	Liquid ammonia q.s. pH 9	
25	Distilled water q.s.	100 g

This gel is colourless and clear and has a viscosity of 2,800 cP, determined with a DRAGGE apparatus,

spindle III.

AEROSOL FOAMS

Example 7g:

	Polymer according to Example 3i	3 g
5	Polyoxyethylenated nonylphenol (containing 9 moles of ethylene oxide) sold under the name "ANTAROX CO 630" by GAF	5 g
	Perfume	0.03g
	Liquid ammonia q.s. pH 9	
10	Distilled water q.s.	100 g
	85 g of this solution are packaged with 15 g of a propellant mixture F114:F12 (43:57) sold under the name "Freons" by DU PONT DE NEMOURS.	

These lotions, gels and aerosols foams are applied to hair which has previously been reduced, subjected or otherwise to a mechanical deformation, for approximately 30 min. at a temperature of approximately 30°C.

After removal, where appropriate, of the means for mechanical deformation, rinsing with water and drying, the hair is soft to touch, and can be disentangled easily by combing or brushing the hair.

SOLUTION

Example 7h:

25	Polymer according to Example 3k	4 g
	Propylene glycol	15 g

At the time of use, this solution in propylene

glycol is mixed with 80 g of water adjusted to pH 9 by adding ammonia.

This solution is applied to the hair which has been previously been reduced and subjected to a mechanical deformation (curlers). After 30 minutes, the curlers  
5 are removed and the hair is rinsed. The curls are soft and easy to comb.

POWDER

Example 7i

10 4 g of polymer prepared according to Example 3k are packaged in the form of a powder. At the time of use, the polymer is dissolved in 96 g of water, the pH of which has been adjusted to 9 by adding ammonia.

The solution obtained is directly applied to the  
15 reduced hair which has not been subjected to a permanent deformation. After allowing the composition to act for approximately 30 minutes, the hair is rinsed with water and then dried. The hair is soft to touch and can be disentangled easily.

7. A method according to claim 1 substantially as described in Example 5a and any one of Examples 5b or 6a to 6j.

8. A composition suitable for use in a method as defined in any one of claims 1 to 7 which comprises at least one polyhaloacetylated polymer in a suitable vehicle.

9. A composition according to claim 8 wherein the polyhaloacetylated polymer is a polychloroacetylated homopolymer or copolymer which is present in a concentration of from 0.5 to 10% by weight relative to the total weight of the composition.

10. A composition according to claim 8 or 9 wherein the vehicle is an aqueous or aqueous/alcoholic solution having a pH of from 7 to 10.

11. A composition according to any one of claims 8 to 10 which additionally comprises at least one pH modifying agent, a perfume, a dyestuff, a preservative, a thickener, a surfactant or a cosmetic polymer.

12. A composition according to claim 8 substantially as described in any one of Examples 7a to 7i.